RIETVELD-BASED QUANTITATIVE ANALYSIS OF MULTIPHASE POWDERS WITH NANOCRYSTALLINE NiAl AND FeAl PHASES

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Abstract. The influence of crystallite size on the quality of Rietveld refinement and on the accuracy of quantitative phase determination by Hill-Howard procedure based on Rietveld analysis was tested. The studies were performed on two four-phase powder samples. The content of phases in both powders was the same and equal to 62.5, 12.5, 12.5, and 12.5 wt.% for NiAl, FeAl, Al_2O_3 and TiC, respectively. The crystallite sizes of all phases are above 100 nm, except for aluminides in sample B for which they are of nanoscale. The crystallite sizes were analyzed by using Williamson-Hall method. The accuracy in content determination of Al_2O_3 and TiC phases was practically the same for both samples and was equal to 4% for Al_2O_3 and 6% for TiC. The presence of nanosize aluminides in the sample worsened this accuracy from 2% to 4% for NiAl and from 2% to 10% for FeAl. The powder morphology was analyzed by SEM method.

1. INTRODUCTION

The studies were performed on materials with intermetallic and ceramic phases of potential wide application especially in the strong corrosive and abrasive environment. The knowledge of the phase content is of crucial importance in material characterization. Using the Rietveld refinement method [1-3] the quantitative phase analysis [4-6] can be performed when all the phases present in the studied material are identified and their chemical composition and their crystal structure parameters can be correctly refined. The main advantage of the quantitative phase analysis based on the Rietveld method is that it incorporates calculations of the whole diffraction pattern and not only the analysis of selected diffraction lines as in the case of more classical methods [7]. The profile parameters of individual diffraction lines were determined using Toraya PRO-FIT procedure applying Pearson VII function for the description of line profiles [8].

The aim of the present work is the analysis of the influence of crystallite size on the reliability of Rietveld refinement and on the accuracy of quantitative phase determination by Hill-Howard [10] procedure based on Rietveld analysis. Multiphase materials with intermetallic phases of crystallite sizes in micro- and nanoscale were applied for testing.

2. MATERIALS AND RESEARCH METHODOLOGY

The two prepared mixtures of four powder phases were applied as tested materials. Nickel and iron aluminides and titanium carbide were prepared by self-propagating high-temperature synthesis (SHS) process whereas aluminum oxide is commercial

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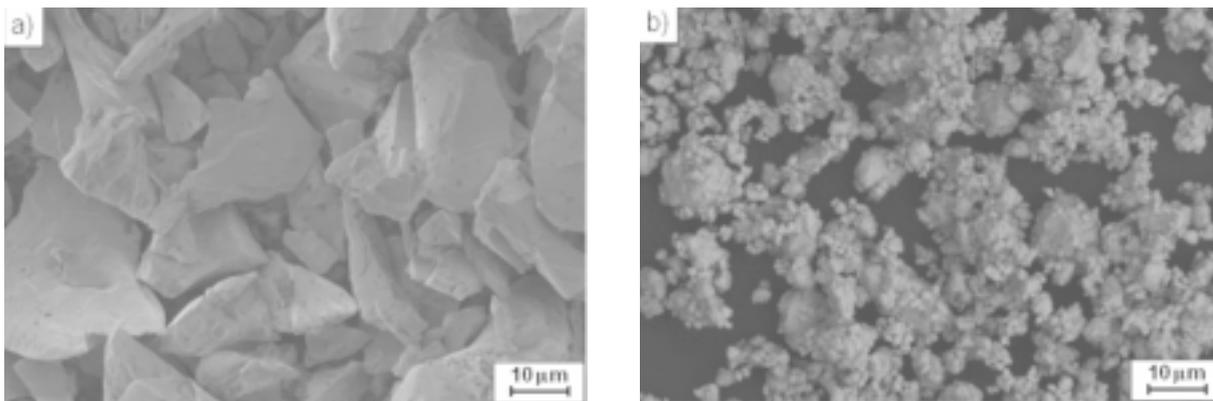Corresponding author: Grzegorz Dercz, e-mail: gdercz@op.pl

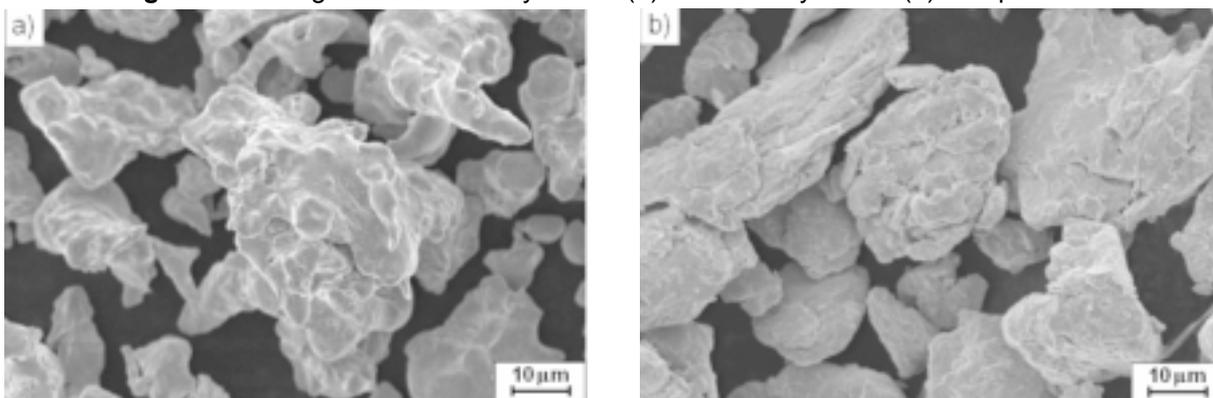**Fig. 1.** SEM images of the microcrystalline (a) and nanocrystalline (b) NiAl powders.

Fig. 2. SEM images of the microcrystalline (a) and nanocrystalline (b) FeAl powders.
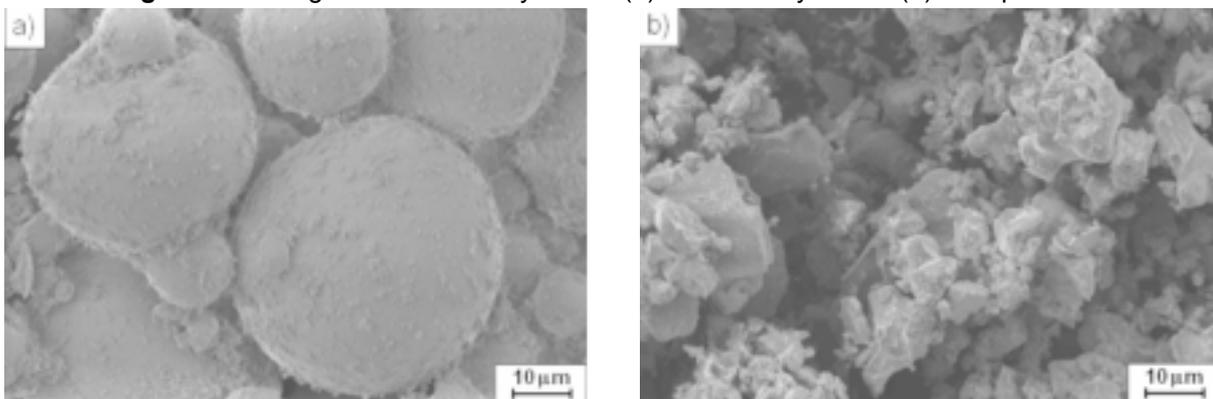

Fig. 3. SEM images of the microcrystalline Al_2O_3 (a) and TiC (b) powders.

material (Albemarle Corp.). The aluminides were ground in Fritsch Pulverisette P5 planetary mill (250 rpm, stainless steel balls of 6 mm diameter, 5:1 ball-to-powder weight ratio, 2 dm³ chamber capacity).

The phase content in both prepared, powder materials were the same and equal to 62.5, 12.5, 12.5, and 12.5 wt.% for NiAl, FeAl, Al_2O_3, and TiC, respectively. The relative weight fractions of phases in a multiphase material can be calculated directly from scale factors as described by Hill and Howard using the following formula:

$$W_p = \frac{S_p (Z \cdot M \cdot V)}{\sum_{i=1}^{n} S_i (Z \cdot M \cdot V)} \cdot 100\%,$$

$$(1)$$

where W_p – relative weight fraction of phase p in the mixture of n phases, (wt.%), S – Rietveld scale factor, Z – number of formula units per unit cell, M
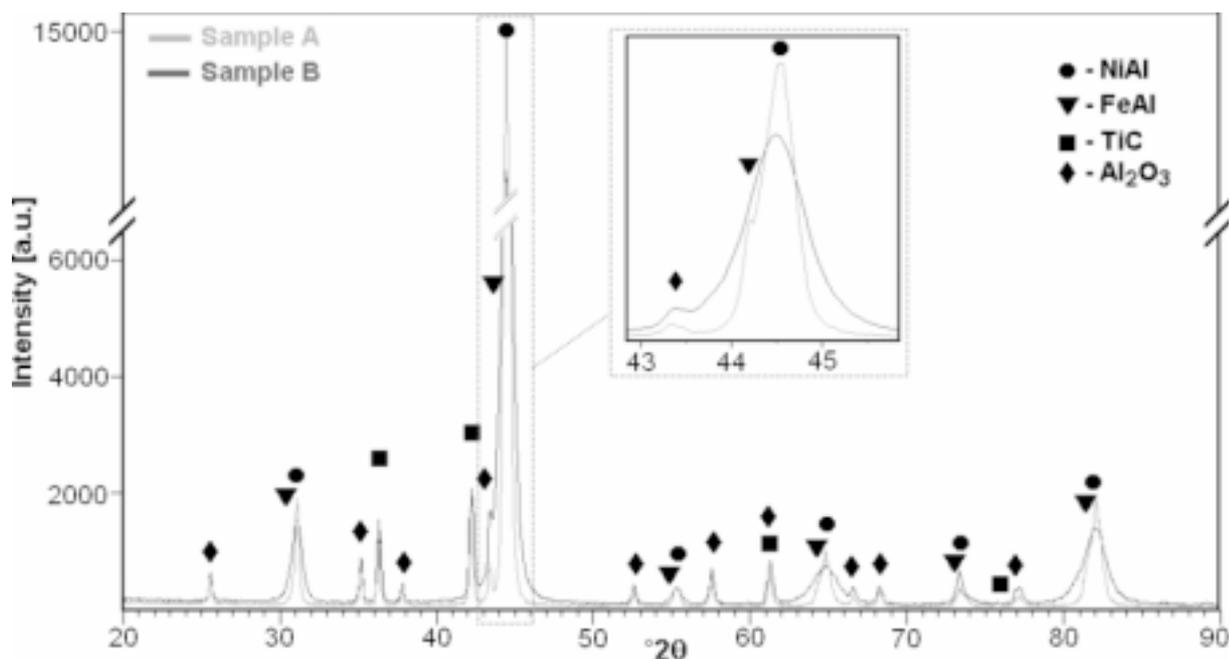
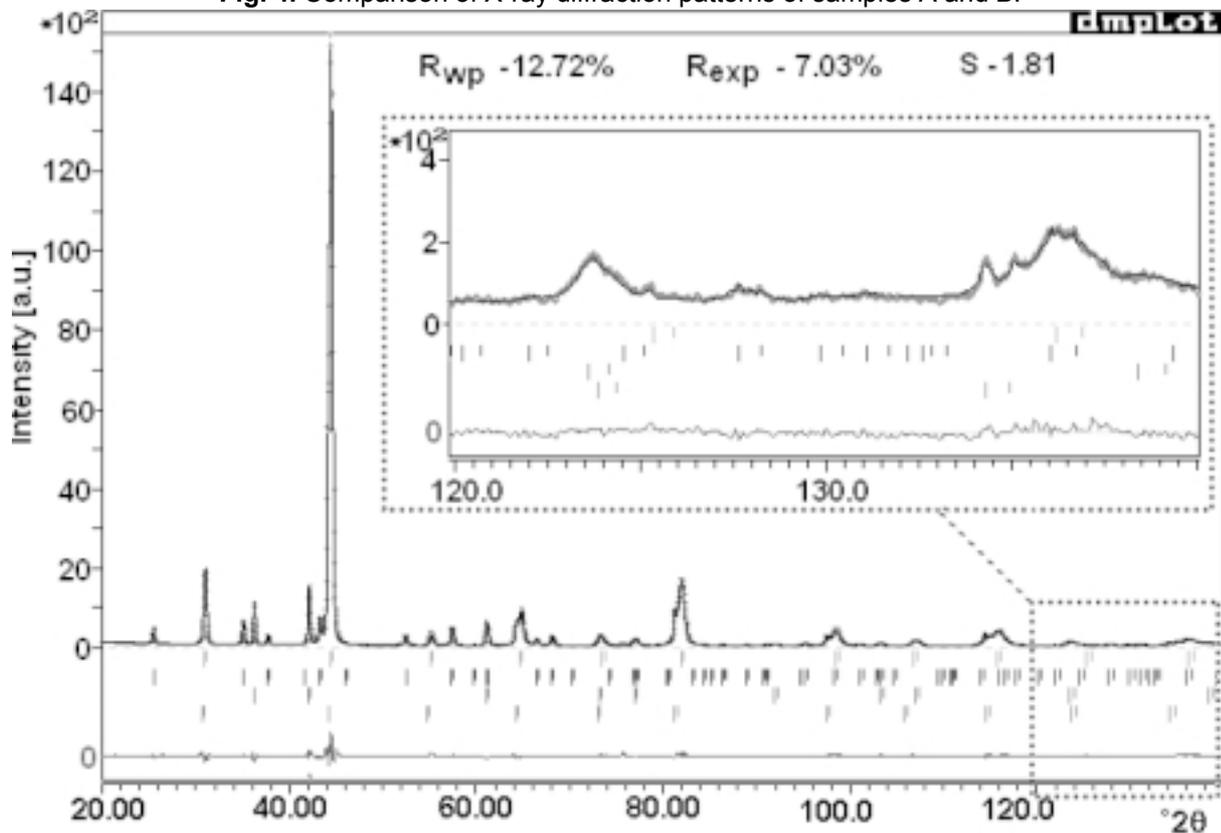**Fig. 4.** Comparison of X-ray diffraction patterns of samples A and B.

Fig. 5. Rietveld output of X-ray diffraction pattern for sample A.

– mass of the formula unit (in atomic mass units), V – unit cell volume (in Å³)

X-ray diffraction patterns were collected using X-Pert Philips diffractometer. Morphologies of the

powders were analyzed using scanning electron microscopy (SEM) method (JEOL JSM-6480). The chemical composition of the powder particles was determined by an energy dispersive spectrometer
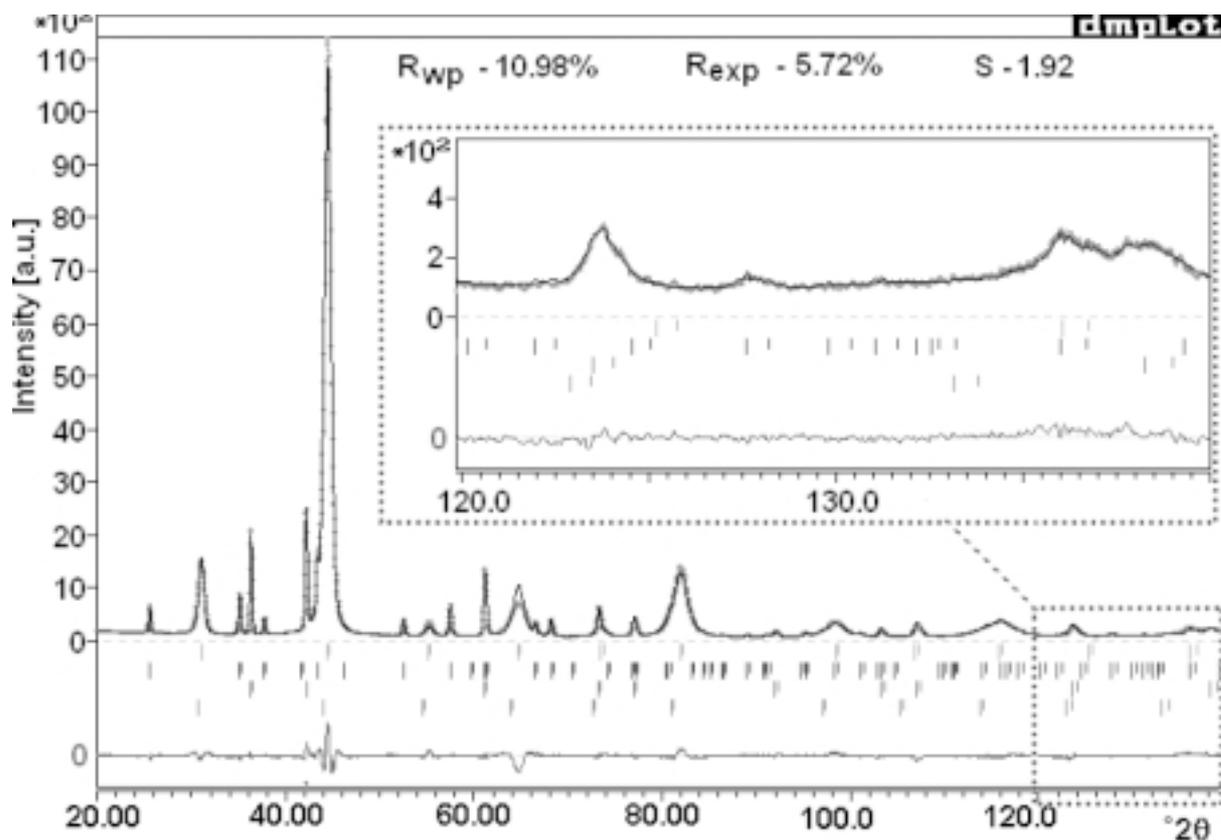
Fig. 6. Rietveld output of X-ray diffraction pattern for sample B.

(EDS IXRF system) using standard calibration method.

3. RESULTS AND DISCUSSION

The SEM images of pure powder components of samples are presented in Figs. 1-3. The morphology of powder particles is quite different. The size reduction of powder particles and their conglomeration during high-energy milling is observed for NiAl powder whereas the size of FeAl particles does not change significantly.

The broadening of diffraction lines was observed for NiAl and FeAl powders ground in high-energy mill. The crystallite sizes determined by Williamson-Hall [9] procedure are equal to 28 nm and 12 nm for NiAl and FeAl, respectively (Table 1); for the other sample components they are above 100 nm. Thus it can be concluded that the powder particles of ground NiAl and especially of FeAl phases are the agglomerates of nanosize crystallites. The aluminum contents in NiAl and FeAl phases determined by EDS method are equal to about 49(2) and 40(2) at.%, respectively.

Comparison of X-ray diffraction patterns for multiphase A and B samples is presented in Fig. 4. The values of goodness of fit parameter *S* for pure components of these samples change from 1.26 for microcrystalline FeAl phase to 1.99 for the nanocrystalline NiAl one. On the other hand the values of this parameter for multiphase A and B samples are equal to 1.81 and 1.92, respectively. Thus the fitting quality of calculated diffraction patterns to experimental ones decreases with the decrease of crystallite sizes to nanoscale (Figs. 5 and 6, Table 1).

The results of quantitative phase analysis are presented in Table 1. The calculated content of NiAl phase are overestimated whereas of the other phases are underestimated in comparison with their nominal contents. The accuracy in content determination of Al_2O_3 and TiC phases was practically the same for both multiphase samples. The strong overlapping of diffraction lines of NiAl and FeAl phases (insert in Fig. 1) can be the reason for the worsening of the accuracy of their content determination. The diminishing of the crystallite size to

nanoscale and lattice distortions also make the accurate determination of phase content more difficult.

4. CONCLUSIONS

· The crystallite sizes of all phases are above 100 nm except for aluminides in the B sample for which they are in the nanoscale.
· The fitting quality of calculated diffraction patterns to experimental ones decreases with the decrease of crystallite sizes to nanoscale.
· The calculated contents of NiAl phase are overestimated whereas of the other phases are underestimated. The accuracy of aluminide content determination decreases with the decrease of crystallite sizes to nanoscale. The content of microcrystalline Al_2O_3 and TiC phases is practically the same for both multiphase samples.
· Lattice distortions and crystallite size distribution as a result of the milling process apart from the strong overlapping of diffraction lines from FeAl and NiAl phases can be the main source of errors in phase content determination of the studied materials.

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